



# Application of Forensic Techniques for Age Dating and Source Identification in Environmental Litigation

Robert D. Morrison\*

*R. Morrison & Associates, Inc., 201 East Grand Avenue, Escondido, CA 92025, U.S.A.*

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A multitude of forensic techniques are available for age dating and source identification, including corrosion models for underground storage tanks, the commercial availability of a compound, chemical associations with discrete types of manufacturing processes, chemical profiling, proprietary additives, stable isotope analysis, degradation models, biomarkers and contaminant transport models. The selection and use of these techniques in environmental litigation must be thoroughly understood and applied to be effective as forensic evidence. When introduced as scientific evidence, the governing assumptions and quality of the data are critically evaluated and frequently successfully challenged. The purpose of this paper is to present an overview of commonly used environmental forensic techniques and their possible applications so that a user can decide which technique or combination of methods is most appropriate for their case.

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## Introduction

The identification of the source of a contaminant release, the timing of the release, and its distribution in the subsurface are common issues in environmental litigation. Forensic techniques used to investigate these issues include underground storage tank corrosion models, identifying the date when a chemical became commercially available, association of a particular chemical with a manufacturing process, chemical pattern recognition (fingerprinting), chemical degradation models and contaminant transport modeling.

## Underground Storage Tank Corrosion Models

The application of tank corrosion models to identify the timing of a liquid release from an underground storage tank (UST) is frequently argued as a means to age date a release. Corrosion models used for underground storage tanks include the Mean Time to Corrosion Failure (MTCF<sup>®</sup>), the Tank Environmental Profiling (TEP<sup>®</sup>) and the Tank Suitability Study (TSS) model (USEPA, 1999b). The Mean Time to Corrosion Failure (MTCF<sup>®</sup>) model is a noninvasive procedure that analyzes corrosion inducing characteristics of an UST site (excavation), and uses statistics to determine the expected leak-free life of the tank. The Tank Environmental Profiling (TEP<sup>®</sup>) technique analyzes hydrocarbon concentrations and other physical and chemical characteristics adjacent to an underground storage tank to determine if it is suitable for cathodic protection. The TSS model is predictive within a specific range of variables that include soil resistivity (3200 to 1,100,000 ohm/cm<sup>3</sup>), total chloride (10 to 343 mg/kg), soil pH (3.6 to 11.4), total sulfide (0 to 48 mg/kg) and total solids (78 to 99.8%). The TEP<sup>®</sup>

and TSS models apply to tanks and not pipelines (USEPA, 1999b).

The MTCF<sup>®</sup> model evolved from an American Petroleum Institute and Petroleum Association for the Protection of the Canadian Environment survey of over 2000 UST sites that were excavated and their condition documented. The study concluded that tank failures due to external corrosion occurred from as early as five years and up to 35 years, and that in the absence of other information, the age of an underground storage tank did not provide a basis to determine the probability of failure due to corrosion (Rogers, 2000). Based on these survey results, a field procedure was developed to obtain the necessary information about the tank backfill material, to allow a statistical estimation regarding the mean time to corrosion failure. The model assumes that uniform and pitting corrosion are the primary corrosion mechanisms, and relies upon tank backfill material properties (e.g. soil moisture content, pH, soil resistivity and sulfide content) and tank age to estimate the probability of failure at any point in time. The mean time to failure for an unprotected carbon steel underground storage tank is described by:

$$\text{age} = 5.75(R^{0.05})(S^{-0.018}) \times \exp(0.13\text{pH}_{\text{soil}} - 0.41M - 0.26\text{Su})$$

where R is the calculated soil resistivity in ohm-centimeter that is obtained from conductivity measurements (which are the inverse of resistivity, or  $R = 1/\text{conductivity}$ ) because conductivity values are reproducible whereas resistivity measurements are operator sensitive, S is the capacity (gallons) of the underground storage tank, M equals 1 if the soil is saturated and 0 if it is not saturated, and Su equals 1 if sulfides are

\*E-mail: bob@rmorrison.com

present and 0 if they are not present (Warren Rogers and Associates, 1981).

The MTCF<sup>®</sup> technique has been applied at in excess of 30,000 sites in the United States. Actual tank removals and physical examinations have reportedly established its accuracy as between 95 and 98% (Warren Rogers and Associates, undated). A study of 800 underground storage tanks at retail service stations in Ohio indicated that at least one tank failure could be expected in 55% of the stations in 15 years, and that failure could be expected at 70% of the stations in 20 years (Garritty, 1996).

### Commercial Availability of a Chemical

The commercial availability of a chemical can bracket the earliest time that a chemical is available for release into the subsurface. Given the multitude of products containing a chemical of interest, the ability to identify commercial synonyms is required. Appendix 1 lists chemical and commercial synonyms for selected chlorinated solvents.

State, Federal and global agreements can provide bases for understanding geographic- or industry-specific chemical usage patterns. The Montreal Protocol was signed in 1987 and amended in June 1990, and local regulations such as Rule 66 are examples. Rule 66 was promulgated by the Los Angeles Air Pollution Control District in July 1966 due to the smog-forming potential of trichloroethylene (TCE) (Molina and Rowland, 1974). Rule 66 required the installation of control equipment if TCE emissions exceeded 40 pounds over 24 h. TCE limits in Los Angeles led, in part, to restrictions in the United States through the Federal Clean Air Act of 1970. This had the consequence that TCE was almost entirely replaced by 1,1,1-trichloroethane (TCA) and tetrachloroethylene (PCE) as the chlorinated degreasing solvent of choice in Los Angeles County from 1967 to 1969 (Archer and Stevens, 1977). As with San Francisco Rule 3, Philadelphia Regulation V and the Clean Air Act Amendments (1990), PCE was determined to be virtually unreactive in the formation of oxidants that contribute to smog and was exempted along with fluorinated hydrocarbons.

The impact of regulations on the operational characteristics of existing equipment and/or chlorinated solvent usage can bracket when a chemical was used at a facility. Given that TCE boils at 184°F, and a steam supply of 15 pounds per square inch at gauge (psig) is required for heating, PCE with 50–60 psig and boiling point of 250°F was not a viable replacement for many types of equipment. TCA with a boiling point of 158°F, however, was a viable replacement in many situations. Equipment originally designed for use with TCA can be utilized with only minor modifications to handle TCE (Dow Chemical Company, 2000b). Table 1 provides examples of the type of historical information available for understanding chemical-specific usage patterns (Morrison, 1998a–b, 2000b, 1999c–d; Doherty, 2000; Pankow *et al.*, 1996).

While information describing chronological transitions in chemical usage is available, extrapolation to a specific site and time period without additional information is difficult. An understanding of who

manufactured a compound of interest during a time interval within a geographic area may, however, provide insight when reviewing historical purchase records to link a particular chemical with a time interval at a facility. Table 2 lists manufacturers of carbon tetrachloride, PCE, TCE and TCA in the United States during the twentieth century.

### Chemical Applications Unique to a Manufacturing Activity

A site's manufacturing processes and material handling systems can provide insight regarding probable locations of a contaminant release. A vapor degreaser, for example, may use solvents only within a discrete boiling range. Obtaining the manufacturer's operating manual or degreaser specifications can therefore provide information concerning the inclusion or exclusion of solvents compatible with a specific degreaser model.

Opportunities exist to associate a unique chemical formulation with a particular activity, such as cold cleaning, for source identification and/or age dating. Compounds used in cold cleaning include aliphatic petroleum compounds (kerosene, naphtha, mineral spirits, Stoddard solvent) chlorinated hydrocarbons (methylene chloride, PCE, TCA, TCE), chlorofluorocarbons, (trichlorotrifluoroethane), alcohols (ethanol, *iso*-propanol, methanol) and other solvents such as acetone, benzene, cellosolve (2-ethoxyethanol) and toluene. Stoddard solvent, mineral spirits and naphtha were used in cold cleaning because of their low cost and relatively high flash point. Alcohols used alone, or blended with chlorocarbons or chlorofluorocarbons, were used for specialty applications such as degreasing activated soldering fluxes (ASM, 1996). Solvent blends were used in cold cleaning to provide improved solvency, reduce cost and to minimize fire hazards. Of these solvents, TCA has been the most widely used (ASM, 1996). Appendix 2 lists common applications for selected chlorinated solvents.

### Age Dating and Source Identification of Chlorinated Solvents

Forensic techniques available for age dating and source identification of chlorinated solvents include additive identification, isotopic analysis and degradation models. Additives blended with chlorinated solvents provide an opportunity to date the timing and/or origin of a solvent release. In most cases, phase-separate product is required for this technique, given the low initial concentrations of additives in the solvents. Additives are blended with chlorinated solvents for the following reasons (Archer, 1984):

- (1) As an acid acceptor that reacts with and chemically neutralizes trace amounts of hydrochloric acid formed during degreasing operations and which may cause corrosion of the part being degreased;
- (2) As a metal inhibitor that deactivates the metal surface and complexes any metal salts that might form. PCE does not require a metal inhibitor while TCE and TCA contain metal inhibitors and acid acceptors; and

Table 1. Chronology of TCE production and usage

Year	Historical information
1864	TCE synthesized by E. Fisher via the reductive dehalogenation of hexachloroethane ( <a href="#">Fisher, 1864</a> ).
1908	TCE production begins in Austria, the United Kingdom and Yugoslavia ( <a href="#">Gerhartz, 1986</a> ).
1909–10	TCE formulated in Germany and production begins in 1910 ( <a href="#">Mellan, 1957</a> ).
1921	Dow Chemical Company synthesizes TCE in the United States ( <a href="#">Doherty, 2000</a> ).
1922–35	Carbide & Carbon Chemicals produce TCE in the United States.
1925	Roessler & Hasslacher Chemical Company synthesize TCE in the United States ( <a href="#">Hardie, 1964</a> ).
1926	TCE manufacturers in the United States include DuPont de Nemours, Carbide & Carbon Chemicals Corporation and Westvaco Chlorine Productions Company.
1928	TCE used to treat trigeminal neuralgia ( <a href="#">Oljenick, 1928</a> ).
1933	TCE considered for use as a general anesthetic.
1934	TCE produced in Japan.
1935–37	TCE mentioned as a poisonous chemical.
1940	TCE used for the extraction of oils from oil seed and as a solvent in the refining of petroleum.
1941–45	United States government controls the manufacture of TCE during World War II. TCE manufacturers include Dow, DuPont and Westvaco Chlorine. TCE is used primarily for degreasing machinery parts ( <a href="#">Lowenheim and Moran, 1975</a> ).
1942	TCE is used as a reagent in synthetic dye production, as an ingredient in glue, insecticides, paint and varnish removers, water proofing compositions, a refrigerating ingredient and as an ingredient in rubber cements.
1943	TCE used in vapor cleaning of motors.
1946	Westvaco Chlorine Products Corporation manufacturers TCE.
1947	In the United States, Dow Chemical Company, DuPont de Nemours, Food Machinery & Chemical Company and Hooker-Detrex manufactures TCE ( <a href="#">Chemical Engineering News, 1950</a> ).
Late 1940s	TCE replaces carbon tetrachloride in metal degreasing and dry cleaning ( <a href="#">Ram et al., 1999</a> ).
1949–55	Niagara Alkali produces TCE ( <a href="#">Chemical Industry, 1949</a> ).
1950s	Hemorrhagic diseases in the early 1950s are traced to animal feed containing TCE-extracted soybean meal. Most manufacturers in the United States voluntarily withdraw soybean oil meals defatted with TCE in 1952 ( <a href="#">Huff, 1971</a> ).
1952	TCE used in the prevention of post-harvest decay of fruits and as a degreasing solvent. About 92% of TCE is consumed in vapor degreasing ( <a href="#">Chemical Week, 1953</a> ).
1954	TCE used in soybean oil extraction. Prior to 1954, amines were the most popular stabilizer used in TCE.
1955	TCE used for vapor degreasing, especially on metallic items with phosphate finishes where strong alkaline solutions cannot be used, and as a freezing point depressant for carbon tetrachloride, usually in fire extinguishers. TCE used as a solvent for crude rubber, dyes, bitumens, pitch, sulfur, oils, fats, waxes, tar, gums and resins.
1956	Annual sales of TCE in the United States are estimated at 250 million pounds ( <a href="#">Kircher, 1957</a> ).
1959–60	DuPont's Niagara Falls facility accounts for half the total United States production of 485 million pounds ( <a href="#">Chemical Engineering News, 1960</a> ).
1966	Rule 66 promulgated which limits TCE emissions in Los Angeles County, California.
1969	TCE production in the United States peaked at 596 million pounds.
1970	TCE used for 82% of all vapor degreasing in the United States. Diamond Shamrock adopts DuPont's use of trade name Triclene ( <a href="#">Chemical Engineering News, 1970</a> ).
1972	Rhode Island bans use of TCE ( <a href="#">Chemical Marketing Report, 1975</a> ).
1974	Major TCE producers in the United States include Dow Chemical, Ethyl Corporation, Occidental Petroleum Company, PPG Industries and Diamond Shamrock (1969–1977). Dow and PPG produce about 70% of total output of TCE in the United States ( <a href="#">Kroschwitz and Howe-Grant, 1991</a> ).
1975	National Cancer Institute reports that massive oral doses of TCE caused liver tumors in mice but not in rats ( <a href="#">NIH, 1982</a> ).
1976	The National Cancer Institute publishes the results of a cancer bioassay that concludes that TCE is an animal carcinogen ( <a href="#">NCI, 1976</a> ).
1977	The United States Department of Agriculture (Food and Drug Administration) bans the use of TCE as a general anesthetic, grain fumigant, skin, wound and surgical disinfectant, a pet food additive, and as an extractant in spice oleoresins isolation, hops and coffee decaffeination. TCE is banned as a food additive and as an ingredient in cosmetic and drug products ( <a href="#">Linak, Lutz and Nakamura, 1990</a> ).
1978	General Foods Corporation stops using TCE for decaffeination of its Sanka and Brim brands of coffee and switches to methylene chloride ( <a href="#">Doherty, 2000</a> ).
1980	Occidental Petroleum Company ceases production of TCE in the United States.
1981	Ethyl Corporation, PPG Industries, Diamond Shamrock, and Hooker Chemical Company synthesize TCE in the United States.
1982	Ethyl Corporation ceases TCE production.
1983	TCE primarily used for vapor degreasing in the automotive and metals industries.
1986	Usage of TCE estimated in the United States as 80% for vapor degreasing, 5% as a chemical intermediate, 5% in miscellaneous uses and 10% exported.
1989	France forbids the sales of TCE to persons under the age of 18 ( <a href="#">European Chlorinated Solvent Association, 2000</a> ).
1991	The use of TCE for metal cleaning and degreasing is estimated at 90% of the total United States production ( <a href="#">Chemical Marketing Report, 1992</a> ).
1996	Sweden prohibits the professional use of TCE although the National Chemicals Inspectorate can admit exceptions ( <a href="#">European Chlorinated Solvent Association, 2000</a> ).
1997	Only Dow Chemical Company and PPG synthesize TCE in the United States ( <a href="#">Chemical Marketing Report, 1997</a> ).

Table 2. Primary manufacturers of four chlorinated solvents in the United States in the 20th century and their approximate manufacturing interval(s) for carbon tetrachloride, TCE, PCE and TCA (after Doherty, 2000)

Manufacturer	Carbon tetrachloride	TCE	PCE	TCA
Allied Chemical & Dye	1955–1981			
Brown Company	1925–1928			
Carbide & Carbon Chemicals		1922–1935		
Diamond Alkali/Diamond Shamrock	1944–1986		1950–1986	
Diamond Shamrock		1969–1977		
Dow Chemical	1908–2000	1921–2000	1923–2000	1936–1994
DuPont Company	1974–1989		1933–1986	
Eastman Kodak	1925–1927			
Ethyl Corporation	1969–1977	1967–1982	1967–1983	1964–1976
Frontier Chemical/Vulcan Materials	1956–2000		1958–2000	
Great Western Electrochemical	1917–1938			
Hooker Chemical/Occidental Chemical		1956–1980	1949–1991	
Hooker-Detrex/Detrex Chemical		1947–1972	1947–1971	
LCP	1981–1991			
Mallinckrodt Chemical Works	1956–1960			
Niagara Alkali		1949–1955		
Niagara Smelting/Staufer Chemical/Akzo	1922–1991			
Occidental Chemical	1987–1994			
Pittsburgh Plate Glass (PPG Industries)	1957–1972	1956–2000t	1949–2000	
PPG Industries				1962–2000
Roessler & Hasslacher Chemical Company/DuPont Company		1925–1972		
Seeley & Company	1941–1943			
Stauffer Chemical			1955–1985	
Taylor Chemical	1933–1944			
Vulcan Materials				1970–2000
Warner Chemical/Warner-Klipstein/Westvaco Chlorine/Food Machinery and Chemical/FMC Corp	1908–1979			
Westvaco Chlorine		1933–1949	1940–1945	

- (3) As an antioxidant that reduces the solvent's potential to form oxidation products. TCE requires an antioxidant (Archer, 1996).

An example of a metal inhibitor is 1,4-dioxane. The addition of 1,4-dioxane to TCA prevents corrosion of aluminum, zinc and iron surfaces. In 1985, 90% of all of the 1,4-dioxane synthesized in the United States was used as an additive in TCA. Producers of 1,4-dioxane included Ferro Corporation, Dow Chemical Company (also imported 1,4-dioxane) and Stephan Company. Other TCA additives include 1,3-dioxolane, glycol-diester, nitromethane, *sec*-butylalcohol, alkanol, *iso*-propylalcohol and toluene. The additives can range in concentration from 3 to 7% in vapor degreasing grades of TCA (Archer, 1984).

The presence of 1,4-dioxane in a soil or groundwater sample may provide an opportunity to distinguish between multiple sources of TCA, and act as a tracer (1,4-dioxane is transported faster than TCA in groundwater). The presence of 1,4-dioxane leading a TCA groundwater plume at the Gloucester chemical-waste landfill near Ottawa, Ontario is such an example. The retardation rate for 1,4-dioxane at the Gloucester landfill was 1.1, while the retardation rate for TCA was greater than 6 (Jackson and Dwarakanath, 1999). When reviewing analytical results for the presence of 1,4-dioxane, it is important to realize that USEPA Method 8240 does not report the presence of 1,4-dioxane, while Method 8260 does. It is therefore important to confirm that the presence of 1,4-dioxane is source-related and not a laboratory artefact (Zemo, 2000).

The low concentrations of most stabilizers must be considered when using stabilizers to identify multiple sources. In most cases, a phase-separate liquid sample provides the greatest opportunity for stabilizer detection, due to the low initial concentrations. If multiple phase-separate plumes of chlorinated solvents have come-mingled, the ability to distinguish between individual sources using additives may be compromised. Knowledge of the original additive package added to the solvent is therefore essential with this technique.

Another factor to consider when using this technique is that the composition of stabilizers and additives varies between operators and possibly solvent manufacturers and/or suppliers. Exceptions include contractual specifications or standards, such as the United States Department of Defense MIL-T-7003 and OT-634C, or ASTM D 4080-96 for TCE. Examples of additives in selected chlorinated solvents are summarized in Table 3 (Kircher, 1957; IARC, 1979; Mertens, 1993; Archer, 1996; Jackson and Dwarakanath, 1999; Morrison, 1999d; Doherty, 2000).

Isotopes are used to distinguish between chlorinated solvent manufacturers, and to identify multiple sources in co-mingled groundwater plumes. Chlorinated compounds are expected to exhibit a wide range of isotopic signatures due to various chemical reactions. Those reactions may include dehydrochlorination or dehydrogenation. Production conditions (e.g. temperature differences, catalysts used, engineering design, etc.) can result in a wide range of isotope fractionation effects that are manufacturer-dependent. A wide range in  $\delta D$  signatures is likely to be associated with different manufacturing processes. These variations are expected



Table 3. Examples of additives in selected chlorinated solvents

Chemical	Additive/Impurity
Carbon tetrachloride (CT)	Technical grade carbon tetrachloride can contain less than 1 mg/L of carbon disulfide if produced by disulfide chlorination, as well as trace amounts of bromine and chloroform (Doherty, 2000). Corrosion inhibitors include alkylcyanamides, diphenylamine, ethylacetate, and ethylcyanides (McKetta and Cunningham, 1979; Kroschwitz and Howe-Grant, 1991).
Chloroform (TCM)	Ingredients may include bromochloromethane, carbon tetrachloride, dibromodichloroethane, dibromodichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, <i>cis</i> - and <i>trans</i> -1, 2-dichloroethene, dichloromethane, diethylcarbonate, ethylbenzene, 2-methoxyethanol, nitromethane, pyridine, 1,1,2,2-tetrachloroethane, trichloroethylene, <i>meta</i> -xylene, <i>ortho</i> -xylene and <i>para</i> -xylene. In Japan, chloroform has a minimum purity of 99.95% and can contain assorted chlorinated hydrocarbons as impurities.
Dichloromethane (DCM)	Stabilizers (0.0001–1%) may include phenol, hydroquinone, <i>para</i> -cresol, resorcinol, thymol, 1-naphthol or amines.
Tetrachloroethylene (PCE)	Early stabilizers included amines and hydrocarbons (Chemical Engineering, 1961). More recent stabilizers include morpholine derivatives, and/or mixtures of epoxides and esters (Gerhartz, 1986).
Trichloroethylene (TCE)	Acetone, acetylenic compounds, aniline, borate esters, <i>n</i> -butane, <i>p</i> - <i>tert</i> -butylcatechol, butylguaiacol, butylene oxide, <i>o</i> -cresol di- <i>iso</i> -propylamine, 1,4-dioxane, epoxy compounds, ethylacetate, hydroxyanisole derivatives, hydrazine derivatives, hydrazones, <i>iso</i> -butyl alcohol (Gerhartz, 1986), <i>iso</i> -cyanates (aliphatic), lactone, nitro compounds (e.g. <i>o</i> -nitrophenol), oxirane, 1-pentanol, phenol, propargyl alcohol, propylene oxide, pyrazoles, pyrazoline derivatives, pyrrole derivatives (Chemical Engineering, 1961), sterates, styrene oxide, sulfur dioxide, tetrahydrofuran, tetrahydrothiophene, thiazoles, thymol and triethylamine. For technical grade TCE, the purity is around 99.97% with no free chloride and stabilizers. Technical grade TCE, TRI-119 and TRI-127 manufactured by PPG Industries, for example, include the anti-microbial agent thymol (0–20 mg/L) and hydrochloro <i>mono</i> -methylether (80–120 mg/L). Antioxidants such as amines (0.001–0.01%) or combinations of epoxides, such as epichlorohydrin and butylene oxide (0.2–2% total) are added to TCE to scavenge any free HCL and AlCl <sub>3</sub> . Analgesic grades of TCE can contain thymol that is often dyed with waxoline blue for identification (Huff, 1971).
1,1,1-Trichloroethane (TCA)	Stabilizers (~3–8%) include nitromethane, N-methylpyrrole, 1,4-dioxane, butylene oxide, 1,3-dioxolane, glycol diesters, <i>iso</i> -propyl alcohol, toluene and <i>sec</i> -butyl alcohol (McKetta and Cunningham, 1979). 1,4-dioxane may be present in TCA at 0–4% by weight. A Material Safety Data Sheet (MSDS) for Solvent 111 <sup>®</sup> lists the 1,4-dioxane concentration as 25 mg/L.

to be great in the narrow range between  $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$  values (e.g. fractionation of  $^{37}\text{Cl}$  occurs during the manufacturing of chlorinated solvents) that is associated with various solvents (Tanaka and Rye, 1991). The low abundance of  $^{37}\text{Cl}$  isotopes found in organic solvents occurs because the  $^{37}\text{Cl}$  atoms are bound more tightly to carbon than are  $^{35}\text{Cl}$  atoms (Bartholomew, Brown and Loundsbury, 1954). The difference in bond strength results in chlorine isotope fractionation due to temperature and pressure differences during the manufacturing of the chlorinated solvents (Tanaka and Rye, 1991).

The isotopic analysis of TCE provides an example of this method. The isotopic composition of ACS-grade trichloroethylene falls within the following range:  $\delta^{13}\text{C} = -48.0$  to  $-27.8^{0/00}$ ,  $\delta^{37}\text{Cl} = -2.54$  to  $+4.08^{0/00}$  and  $\delta\text{D} = -30$  to  $+530^{0/00}$ . The heavy hydrogen isotope composition of TCE is believed to be a function of isotope fractionation associated with the chemical synthesis reactions used to produce TCE. Differences in the isotopic composition are dependent upon whether the TCE is produced as a by-product of the high-temperature chlorination of ethene or of 1,2-dichloroethane, via the chlorinolysis of propane, other light hydrocarbon feedstock or their partially chlorinated derivatives, or by the oxychlorination of ethene (Kroschwitz and Howe-Grant, 1991). Chemical reactions that produce isotopically light hydrochloric acid result in other chemical products becoming isotopically enriched because the yields for those reactions are engineered to be high. Dehydrochlorina-

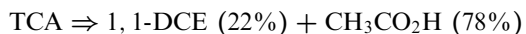
tion reactions are common in the industrial production of many chlorinated hydrocarbons. As a result, many chlorinated hydrocarbons will have isotopically enriched  $\delta\text{D}$  signatures. In one case, the use of isotopic ratios for  $^{13}\text{C}/^{12}\text{C}$  and  $^{37}\text{Cl}/^{35}\text{Cl}$  was used to distinguish between three manufacturers of PCE, TCE and TCA (Van Warnerdam *et al.*, 1995).

Dehydrogenation and dehydrobromination reactions may produce isotopically enriched compounds, since  $\text{H}_2$  and  $\text{HBr}$  are isotopically depleted relative to other hydrogen compounds. It is unlikely that dehydrofluorination would produce isotopically enriched compounds, because hydrogen fluoride exhibits relatively small fractionation effects versus other hydrogen bearing compounds.

Issues associated with the interpretation of isotopic data include the quality of the extraction process, especially if one solvent is extracted from a mixture of compounds. Interpretation of the isotopic data may also be biased due to the potential for isotopic fractionation in the subsurface, as well as due to the precision of the gas chromatography-isotope ratio/mass spectrometric (GC/IR/MS) measurements (Philp, 1998b; Stout, Uhler and McCarthy, 1999).

The presence of chlorinated solvents and degradation patterns unique to a parent compound has been used for age dating (Brugger and Lehmicke, 2000). Of these methods, an approach describing the hydrolysis of TCA to 1,1-dichloroethene (1,1-DCE) is commonly encountered (Feenstra, Cherry and Parker, 1996). The groundwater temperature (yearly average), and

the TCA and 1,1-DCE concentrations are required for the model (Smith, 1999). This method assumes that the molar hydrolysis relationship is:



and that the TCA and 1,1-DCE concentrations are known with a great degree of accuracy and precision. The age of the TCA in the groundwater is then approximated by (Smith and Eng, 1997; Smith, 1999; Murphy and Gauthier, 1999):

$$t = 2.88 \times 10^{-21} \exp[55.604/(1 + 2.175 \times 10^{-3}T)] \times \ln[1 + 6.25(C_D/C_T)]$$

where  $t$  is the time in years since TCA entered the groundwater,  $C_D$  is the 1,1-DCE groundwater concentration in mg/L,  $C_T$  is the TCA groundwater concentration in mg/L, and  $T$  is the groundwater temperature in degrees Fahrenheit. The contaminant migration rate is then determined by dividing the horizontal distance to each well by the age of the TCA in the well.

### Age Dating and Source Identification of Petroleum Hydrocarbons

Forensic techniques employed to age date and identify source areas of petroleum hydrocarbons include chemical fingerprinting, proprietary additives, alkyl-leads, oxygenates, dyes, stable isotope analyses, weathering patterns, biomarkers and degradation models.

Chemical fingerprinting offers the ability to distinguish the type of hydrocarbon (diesel, gasoline, jet fuels, kerosene, Stoddard solvent, etc.) in the identification of the source and/or timing of a release (see Figure 1). This identification can be performed through pattern recognition, or with pattern matching of gas chromatographic traces from different samples, or it can be accomplished qualitatively with intrusive testing such as cone penetrometry (CPT) that is equipped with a laser-induced fluorescence sensor (Kram, 1988).

Compounds that are used in pattern recognition analysis include light petroleum products (BTEX, heavier aromatics and alkyl-paraffins), diesel fuels and distillates (normal alkanes and isoprenoid paraffins), biomarkers such sesquiterpanes ( $C_{15}$ ), diterpanes ( $C_{20}$ ), triterpanes ( $C_{30}$ ), steranes ( $C_{30}$ ) and hopanoid compounds (i.e. present in some petroleum products but not creosote) (Butler, 1999), crude oils and heavy fuels (substituted polyaromatic hydrocarbons) and thiophenes (Harvey, 1997; Stout, Uhler and McCarthy, 1999; Stout, 1999).

### Proprietary Additives

Proprietary additives are blended with refined products. Additive packages are often associated with a discrete time period or fuel. The polybutene additive that is present in Chevron detergent F-310, for example, was marketed in 1982. The use of additives for hydrocarbon fingerprinting requires a prior knowledge of the additive package as well as the ability to

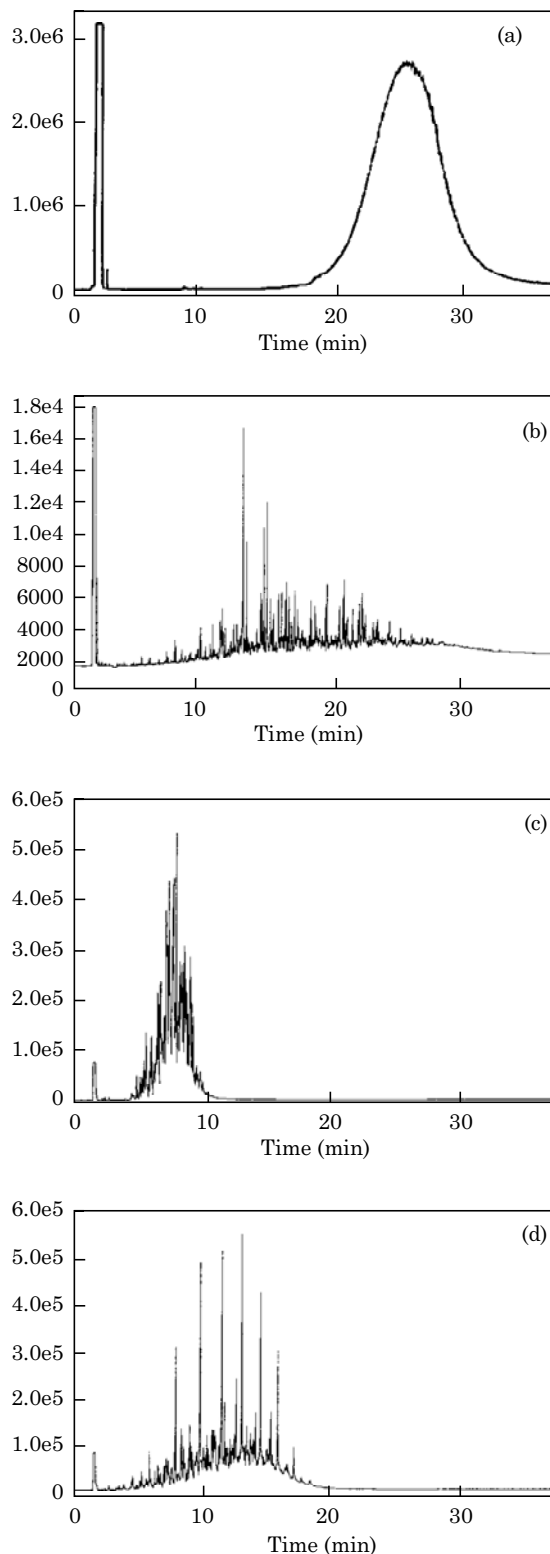


Figure 1. Chromatograms for (a) motor oil, (b) Bunker C oil, (c) Chevron 325 gasoline and (d) kerosene (reprinted with permission of Friedman & Bruya, Seattle, Washington).

detect a unique additive that is not obscured by other chemicals or environmental degradation products. The composition of additive packages for refined products varies with time. A typical additive package for gasoline formulated in the 1980s, for example, included tetraethyl-lead, ethylene dibromide and inactive ingredients, such as stability enhancers, dyes and anti-oxidants (Younglass *et al.*, 1985).

Table 4. Chronology of lead usage in gasoline

Date	Significant events in lead usage in gasoline
1853	C. Lowig reacts a lead-sodium alloy with ethyl iodide and obtains an impure hexaethyldi-lead from which a few triethyl-lead salts are prepared (Nriagu, 1990).
1921	On December 9, 1921, Thomas Midgley and Tom Boyd of General Motors Research Corporation discover that tetraethyl-lead ( $\text{Pb}(\text{C}_2\text{H}_5)_4$ ) is an effective antiknock additive (Nickerson, 1954).
1923	Gasoline with tetraethyl-lead (also referred to as lead tetraethide and tetraethylplumbane) is dispensed on February 2, 1923, at a Refiners Oil Company service station in Dayton, Ohio (Nriagu, 1990; Rhue <i>et al.</i> , 1992). Tetraethyl-lead is the only antiknock agent used until 1960 (Kaplan <i>et al.</i> , 1997; Kaplan, 2000). The Kruase-Callis process for the large scale production of $\text{Et}_4\text{Pb}$ is patented and involves combining molten sodium and lead that is autoclaved with ethyl chloride or methylene chloride to form tetraethyl-lead or tetramethyl-lead.
1924	In August of 1924, General Motors and Standard Oil Company of New Jersey (now Exxon Corporation) form Ethyl Gasoline Company (now Ethyl) to market tetraethyl-lead.
1926	The United States Surgeon General recommends 3.17 grams/gallon ( $\sim 2,700$ mg/L by weight) as the maximum allowable concentration of tetraethyl-lead per an agreement with Ethyl Corporation (Kaplan <i>et al.</i> , 1997).
1927/28	The lead scavengers ethylene dibromide and ethylene dichloride are introduced (Nickerson, 1954).
1947	Ethyl Corporation begins marketing TEL at the end of 1947.
1948	DuPont Corporation markets TEL.
1950	Most gasoline in the United States contains tetraethyl-lead.
1959	The maximum permitted lead in gasoline increases to 4.23 grams/gallon (Gibbs, 1990).
1960	In 1960, tetramethyl-lead and trimethyl-lead (marketed by Standard Oil Company of California, now Chevron Corporation) is introduced (Stormant, 1960; Rhue <i>et al.</i> , 1992; Kaplan <i>et al.</i> , 1997). Tetraalkyl-lead (TAL) is added to commercial gasoline in the United States to improve the octane rating (Messman and Rains, 1981).
1969	<i>tertiary</i> -butylalcohol (TBA) is introduced by ARCO (Peterson, 2000). Consumption of lead alkyls peaks in 1969 and declines throughout the 1970s as improvements in catalytic reforming, hydrocracking and hydrotreating occurs (Global Geochemistry Corporation, 1991 (now Zymax); Lee <i>et al.</i> , 1992; Rhue <i>et al.</i> , 1992). For premium grade gasoline, lead concentrations are as much as 2.9 grams per gallon.
1970	Gulf Oil Company (now Chevron) introduces low leaded gasoline (Harvey, 1998).
1972	In April, Japan markets lead-free gasoline.
1973	EPA defines unleaded gasoline as gasoline containing not more than 0.05 grams of lead per gallon and not more than 0.005 of phosphorus per gallon.
1974	EPA requires major gasoline retailers to sell one grade of unleaded gasoline by July 1, 1974 (Harvey, 1998).
1975	EPA calls for the reduction of lead in automobile gasoline to 1.7 g/gal in 1975
1979	Average lead content of gasoline (total of leaded and unleaded gasoline) is set at 0.8 g/gal for large refiners and up to 2.65 g/gal for small refiners depending on the refinery size (Gibbs, 1990). Small refiners are defined as those with less than 50,000 barrels per day that are not owned or controlled by large companies.
Late 1970s/ Early 1980s	Only DuPont, PPG, Ethyl and Nalco manufacture tetraethyl-lead in the United States.
1980	EPA establishes the overall lead content for large refiners at 0.5 grams of lead per gallon effective October 1, 1980 (Gibbs, 1990). Tetraethyl-lead is reportedly the only alkyl-lead additive added to gasoline after 1980 (Hurst, Davis and Chinn, 1996) although other literature suggests that the phasing out of tetraethyl-lead continued into the early 1980s (Clark, undated; Kaplan, 2000; Peterson, 2000).
1982	EPA sets the average lead concentration in gasoline at 0.10 grams of lead per gallon for large refiners effective November 1, 1982 (Gibbs, 1990; Harvey, 1998).
1985	EPA limits the concentration of lead to 0.50 grams per gallon in July of 1985 (Gibbs, 1990). Lead credits are allowed (Harvey, 1998). Many states begin phasing out lead in the gasoline during the middle to late 1980s.
1986	EPA limits lead content to 0.10 grams per gallon for leaded gasoline manufactured by refineries on January 1986 (Gibbs, 1990). Lead credits are allowed (Harvey, 1998).
1987	Only tetraethyl-lead used in gasoline (Kaplan, 2000).
1988	EPA eliminates lead credits (Harvey, 1998).
1990	Clean Air Act Amendments regulate alkyl-lead compounds by prohibiting the use of leaded gasoline for on-road vehicles (USEPA, 1999c). Fuels for competitive use vehicles are exempted.
1992	California eliminates the production of leaded gasoline (Kaplan <i>et al.</i> , 1997).
1995	Over 50 countries (20 in Africa) permit lead in gasoline at concentrations up to 0.8 g/L. The maximum lead concentration in Europe is 0.15 g/L.
1996	EPA eliminates lead in all gasoline (per Section 211(n) of the Clean Air Act) (Harvey, 1998).

Gasoline fuel additives often contain oxygen in their molecular structure. As a result, the additives are usually water-soluble and biodegradable. Many additive polymers also tend to depolymerize into their respective monomers, making it difficult to identify the

parent compound (Galperin, 1997). Refineries purchase additive packages from specialty companies with little or no chemical alteration by the refinery. As a result, identical additives may be present in the parent compounds of a co-mingled fuel plume, complicating

the ability to use constituents in the additive package for source identification (Kram, 1988; Gibbs 1990, 1993; Kaplan *et al.*, 1997; Harvey, 1997; Ethyl Corporation, 1998; Morrison, 1999c,d).

Diesel and jet fuels also contain additive packages. Additive packages for diesel include quality-enhancing packages such as diesel ignition and stability improvers, anti-statics, corrosion inhibitors and surfactants. All of these additives are associated with discrete periods in time. Individual diesel sources can be distinguished by analyzing the sulfur content of the diesel, which usually differs depending on the source of the crude oil. Another way to distinguish diesel fuels is to perform a peak-to-peak comparison of chromatograms from PNA analysis of the samples being compared. Evaluation of PNA and sulfur test results often provides the basis for distinguishing between multiple diesel sources. The identification of biomarkers, such as isoprenoids, can also be used to distinguish differences between fuels. PNA analysis can assist in defining the relative age or use of motor oil since used motor oil contains more PNAs than a pristine sample of the same oil.

## Alkyl-Leads

Chronologies based on gasoline additives and/or gasoline production specifications (i.e. ASTM-D-439 in 1940, ASTM-D-4814 for unleaded gasoline in 1989, and ASTM-D-4814 for unleaded gasoline in 1995) are used for age dating a gasoline release (Bruya, 2000). Alkyl-leads include tetra-alkyl-lead (TAL), tetraethyl-lead (TEL), tetramethyl-lead (TML), trimethyl-lead chloride (TriML), triethyl-lead chloride (TriEL), dimethyl-lead chloride (DiML), methyltriethyl-lead (METL), dimethyldiethyl-lead (DMDEL), trimethylethyl-lead (TMEL) and diethyl-lead chloride (DiEL) (Messman and Rains, 1981; USEPA, 1999b). Table 4 lists significant changes in the use of lead (Gibbs, 1990, 1993; Harvey, 1998; Morrison, 1999c, 2000a,b).

Tetraethyl-lead, triethylmethyl-lead, methyldiethyl-lead and tetramethyl-lead are the most common organic alkyl-lead additives. Lead additive packages often contain multiple combinations, as well as redistribution reaction mixtures, of tetraethyl-lead and trimethyl-lead. Redistribution reactions of equimolar amounts of tetraethyl-lead and tetramethyl-lead can produce trimethyl-lead, trimethylethyl-lead, dimethyldiethyl-lead and methyltriethyl-lead (Christensen and Larson, 1993). Reacted mixtures of leads are typically marketed as RM25, RM50 and RM75, with the number designating the molar percent of trimethyl-lead present (Stout *et al.*, 1999b). A typical commercial reaction mixture from equimolar amounts of tetraethyl-lead and trimethyl-lead is 3.8% trimethyl-lead, 23.4% trimethylethyl-lead, 42.4% dimethyldiethyl-lead, 25.6% methyltriethyl-lead and 4.8% triethyl-lead (Kaplan *et al.*, 1997).

Tetraethyl-lead is a historical gasoline additive that was used to suppress pre-ignition and improve the octane rating. Older gasoline contained tetraethyl-lead, along with lead scavengers such as ethylene dibromide and ethylene dichloride (1,2-dichloroethane). Tetraethyl-lead is usually clear, unless red, orange and/or

blue dyes are added. Prior to 1985, tetraethyl-lead was blended with gasoline at concentrations of about 400 to 500 mg/L. The presence of organic lead in a phase-separate gasoline may therefore be indicative of a pre-1985 release. A complication in using 1985 for age dating and source identification is that tetraethyl-lead is still used in aviation fuels (Avgas). Currently, only TEL is used in aviation fuels, while other aviation fuels such as Jet kerosene and JP-4 do not contain alkyl-lead compounds. For example, Avgas 80/87 has the lowest lead content at 0.5 grams of lead per gallon of fuel, while Avgas 100/130 is a higher octane grade aviation fuel with about 4 grams of TEL per gallon of fuel (USEPA, 1999c). Fuels used for boat and car racing also contain alkyl-lead. RAD racing fuel (RAD 110), for example, contains 4.5 grams of lead per gallon of fuel (USEPA, 1999c). Tetraethyl-lead is not present in condensate, distillates or naphtha (Bruce and Schmidt, 1994; Schmidt, 1998).

The concentration of organic lead in the subsurface is frequently argued as evidence for age dating a release. In 1982, the maximum lead concentration in gasoline was 4.2 grams per gallon. In 1984, the United States Environmental Protection Agency (USEPA) set a maximum of 0.1 gram lead per gallon of gasoline. This concentration applies to the average quarterly production from a refinery or pool standard. The pool standard is the total grams of lead used by a refinery in a given time period, divided by the total amount of gasoline manufactured in the same time frame. As a result, individual batches of gasoline can contain 4.2 grams per gallon per USEPA requirements, and 0.8 grams per gallon in California.

The lead concentration of an individual sample is not conclusive evidence for age dating a release because the lead content for any point in time is based on the pool standard that can vary from batch to batch. The pool standard may not reflect any true refinery amount due to lead accounting practices (lead credits are bought or sold), and because the lead credits are usually averaged quarterly. In addition, multiple releases of gasoline from 1985 to 1991 with low lead concentrations could result in an accumulated lead concentration of 0.5 grams per gallon, and so the presence of lead would not necessarily be evidence of a pre-1985 gasoline release. Another issue in using lead concentrations for age dating based on chronological changes in lead additive packages is that lead can be present in unleaded gasoline at concentrations ranging from tens to hundreds of parts per billion. This lead is believed to originate from the crude oil and refining process (Hurst, 2000). Given that alkyl-leads, such as tetraethyl-lead, have low water- but high organic-solubilities, they can reside in soil after the fuel has evaporated and/or biodegraded. Conversely, tetraethyl-lead can be re-mobilized and dissolved by a subsequent gasoline release that may or may not contain lead.

## Lead Scavengers

The presence of lead scavengers in environmental samples is frequently cited as a means to age date or identify the origin of a gasoline release. In most



forensic applications, the combination of ethylene dibromide (EDB) and/or ethylene dichloride (EDC) with alkyl-leads can be used for source identification. EDB and EDC were introduced in 1928 to minimize the precipitation of lead oxide within automobile engines (Kaplan *et al.*, 1997). During engine combustion, the EDB or EDC forms lead bromide or lead chloride; both of which are relatively volatile and pass through the engine with the exhaust. EDB and EDC concentrations in leaded gasoline have changed over the years and may be present individually or together in the lead additive package (Peterson, 2000). EDB is currently used in aviation piston engines.

## Oxygenates

Oxygenates are blended with gasoline to increase the oxygen content and reduce carbon monoxide emissions. An oxygenate is defined by the American Society of Testing Methods (ASTM) as “An oxygen-containing, ashless, organic compound, such as an alcohol or ether, which can be used as a fuel or fuel supplement” (Gibbs, 1998). From toxicological and forensic perspectives, methyl-tertiary-butyl ether (MTBE) is an oxygenate of great interest in the United States. Atlantic Richfield Company (ARCO) synthesized MTBE in 1979 via the catalytic reaction of *iso*-butylene and methanol. Its documented use on the East Coast is post 1979, and in California it was used after 1986 (Davidson and Creek, 2000). MTBE usage increased by about 40% per year in the 1980s (Sufita and Mormile, 1993; Steffan *et al.*, 1997), and by 1992 the production capacity and actual production of MTBE in the United States were 11.6 and 9.1 billion pounds, respectively. By 1993, MTBE was the most widely used oxygenate, and the second most produced organic compound in the United States (Reisch, 1994).

MTBE was initially added as an octane-enhancing replacement for tetraethyl-lead. MTBE was later used as a fuel oxygenate to decrease the amount of carbon monoxide in automobile emissions and to improve gasoline's tolerance for moisture. MTBE is blended with reformulated gasoline for severe ozone non-attainment areas that do not meet Federal ozone ambient air quality standards. MTBE is not, however, present in all post-1980 gasoline. Starting in 1992, it has been used in gasoline in over 15 states, to meet Federal Clean Air Act of 1990 requirements for oxygenates in wintertime gasoline, and in Federal reformulated gasoline in 1995, to meet carbon monoxide ambient air quality standards (CAEPA, 1996). Table 5 presents an oxygenate chronology (Harvey, 1998; Gibbs, 1998; Morrison, 1999b).

Pure MTBE is about 25 times more soluble in water than benzene (~42,000 mg/L), is considered recalcitrant to biodegradation, and is not retarded by soil as it travels in groundwater (Finneran and Lovely, 2000). As a result of these properties, MTBE is often detected in soil and groundwater. Of the 5738 sites monitored by the California State Water Resources Control Board in 1988, 3180 (55%) groundwater sites had MTBE detected. The persistence and frequency of MTBE detection, therefore, provides opportunities for its use as a surrogate tracer and for age dating and/or source identification. When using MTBE for these purposes,

it is important to identify potential sources of bias that may impact data interpretation including:

- potential false positives with USEPA Method 8020/21 as methyl-pentanes and pentanes co-elute with MTBE (Rhodes and Verstuyft, no date; Uhler, Stout and McCarthy, 2000; Davidson, 2000);
- contributions from non-point sources (Delzer *et al.*, 1996);
- incidental blending and/or mixing of additives in gasoline supplies as gasoline is exchanged or traded among producers to meet contract requirements and to improve transportation logistics;
- cross contamination from one fuel to another, especially in pipelines, tanks and tanker trucks (Robbins *et al.*, 1999);
- seasonal differences in MTBE concentrations; and
- product swapping by the gasoline jobbers or via exchange agreements between refineries or bulk storage facilities (Hitzig, Kostecki and Leonard, 1998).

Given MTBE's high vapor pressure (245 mmHg at 25°C) and solubility in water, its presence in groundwater may not be indicative of a liquid release. MTBE in groundwater may originate as a vapor cloud or as a non-point source, especially when detected at concentrations less than 10 µg/L (Pankow *et al.*, 1997). Non-point sources include storm water runoff (0–15 µg/L) and surface water sources such as watercraft (0–40 µg/L) (Davidson, 1999). The United States Geological Survey (USGS) detected MTBE in 6.9% of 592 water samples collected from storm water in 16 cities and metropolitan areas at concentrations ranging from 0.2 to 8.7 µg/L (Delzer *et al.*, 1996). Eighty-three percent of the MTBE detections occurred in storm water collected during the October through March season of each year (1991–1995), which corresponded to the seasonal use of oxygenated gasoline in areas where carbon monoxide exceeded established air-quality standards.

Cross-contamination of fuels by MTBE complicates the use of MTBE for forensic analysis. MTBE has been detected in the presence of jet fuel, diesel fuel, heating oil, aviation gas and waste oil (Hitzig, Lostecki and Leonard, 1998). In Connecticut, 27 out of 37 heating oil-spill sites had MTBE detected in groundwater at concentrations ranging from 1 to 4100 µg/L, five out of five diesel-contaminated samples contained MTBE, and 26 out of 26 heating oil-contaminated samples contained MTBE (Davidson, 1999). In Maine, 15% of the private wells sampled had MTBE detections, with apparently no gasoline release from an underground storage tank having occurred (Davidson, 2000).

## Stable Isotope Analysis

Radioactive isotopes can provide a means for source identification of petroleum hydrocarbons (Mansuy, Philip and Allen, 1977). Stable carbon isotope compositions, for example, can be used to distinguish between gases from different sources, and whether they are microbial or thermogenic in origin (Philp, 1998a). Other applications include source identification for crude oil.

Table 5. Chronology of oxygenate usage

Date	Description of oxygenate usage and history
1842	MTBE synthesized by English chemist (Faulk and Gray, 2000).
1907	<i>tertiary</i> -Amyl Methyl Ether produced.
1930	Agrol and Alkyl Gas (ethanol fuels) used in Nebraska.
1935	<i>tertiary</i> -Alkyl Ether synthesis patent in the United States is issued.
1937	Germany uses methanol (Harvey, 1998).
1940	Alkyl-Gas (ethanol blend) marketed in Nebraska.
1943	Patents relating to MTBE filed (U.S. Patent No. 1,968,601)
1950s	American Petroleum Institute (API) literature references the applicability of using MTBE in gasoline (Drogos, 2000).
1968	Chevron performs a taxicab field test with gasoline containing MTBE/TAME.
1969	ARCO Corporation blends <i>tertiary</i> -Butyl Alcohol in gasoline (Harvey, 1998; Peterson, 2000; Drogos, 2000).
1973	MTBE used in commercial gasoline in Italy.
1977	Nebraska Gasohol (ethanol blend) program commences.
1978	EPA waiver issued for 10% by volume for ethanol (Gibbs, 1998). First Gasohol (ethanol) station in Nebraska. Arco markets Oxinol (methanol) (Harvey, 1998).
1979	MTBE produced by ARCO Corporation in the United States (Harvey, 1998; Davidson <i>et al.</i> , 2000; Bruya, 2000). EPA waiver issued for 7% volume for MTBE and 2.5% each for methanol and <i>tertiary</i> -Butyl Alcohol (TBA). MTBE included in gasoline in the eastern seaboard, New England, and New Jersey from 1979 to the mid-1980s (McKinnon and Dykson, 1984; Garrett, Moreau and Lowry, 1986). Sun Oil Company receives a waiver from EPA allowing the use of 2.75% by volume methanol along with 2.75% by volume <i>tertiary</i> -Butyl Alcohol in unleaded gasoline (Gibbs, 1990).
1980s	Experimentation with MTBE, methanol (M85) and ethanol as octane boosters conducted in the early 1980s (Harvey, 1998). EPA Substantially Similar Rule issued with 2% by weight oxygen maximum limit (11% by volume for MTBE).
1982	Documented use of MTBE on the East Coast of the United States (Kaplan <i>et al.</i> , 1997).
1988	Denver begins first wintertime oxygenated gasoline program in the United States using MTBE to reduce vehicle carbon monoxide emissions (ethanol subsequently used) (API, 1998; Harvey, 1998). EPA waiver issued for 15% by volume for MTBE as the maximum amount; MTBE is among the top 50 chemicals manufactured in the United States (Uhler, Stout and McCarthy, 2000).
1989/90	Phoenix, Las Vegas, Reno and Albuquerque begin wintertime oxygenated gasoline program using MTBE (ethanol used later). Clean Air Act Amendments enacted. The Substantially Similar Rule maximum oxygen limit increased to 2.7% by weight (15% by volume for MTBE).
1992	Oxygenates required during the winter in carbon monoxide non-attainment areas. Ethanol used where economical. Federal wintertime oxygenated gasoline program requires 2.7% by weight minimum oxygen in 39 carbon monoxide non-attainment areas.
1993	<i>tertiary</i> -Amyl Methyl Ether and Ethyl- <i>tertiary</i> -Butyl Ether usage comes into general use (Peterson, 2000). Reformulated gasoline used in ozone non-attainment areas. Federal reformulated gasoline program requires 2.0% by weight minimum oxygen content. 95% of all gasoline sold in California contains MTBE. MTBE is the most widely used oxygenate in the United States (Reisch, 1994).
1995	TAME added to California fuels since 1995 (California Regional Water Quality Control Board, 1997).
1997	Approximately 8 billion kilograms of MTBE is produced in the United States (Hitig, Kostecki and Leonard, 1998).
1998	California Health and Environmental Assessment of MTBE report recommends the gradual phase-out of MTBE in California gasoline. Approximately 3.8 billion gallons of MTBE used in the United States (Drogos, 2000).
1999	Chevron and Tosco begin gradual phase-out of MTBE in unleaded gasoline. Town of South Lake Tahoe, California bans MTBE because of concerns about its potential impact on the town's drinking water supply.
2000	California bans the use of MTBE with a complete phase-out by December 31, 2002 (Brown and Clark, 1999). California Department of Health Services establishes an MCL for MTBE at 13 µg/L; a secondary MCL standard is set at 5 µg/L, effective on May 18, 2000.

Lead radioactive isotopes are usually reported as ratios using the delta notation ( $\delta$ ). Isotope ratios are given a negative notation if the sample value is lower than the standard value (arbitrarily given as 0%) or a positive notation if the sample ratio is greater than the standard value. The stable isotopes of lead occur in different ratios depending upon the geologic formation from which they were mined. American ores, for example, have  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios as high as 1.31, while Australian and Canadian ores have ratios of approximately 1.04 and 1.06, respectively.

Lead ratios used for age dating and source identification include  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  (Hurst, Davis and Chinn, 1996). High precision lead isotope ratio analysis is used to calibrate these changes in the lead isotope ratios as a function of time. This method is

usually based on  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios; when plotted as a function of time between the late 1960s and the late 1980s as tetraethyl-lead, a systematic trend is observed as a result of manufacturers shifting their lead supply source. Hurst, Davis and Chinn (1996) plotted  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios between 1960 and 1990, and observed distinct ratio differences for different years.

The Anthropogenic (i.e. gasoline-derived) Lead Archeostratigraphy Model (ALAS) is an example of a lead isotope model used to distinguish between multiple sources of dispensed gasoline (Hurst, Davis and Chinn, 1996). The technique is based on the observation that the average stable isotope ratio of leaded gasoline is relatively uniform over intervals of about one year. From 1964 to 1990, the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in United States gasoline and aerosols were

measured, thereby providing a characteristic isotopic signature (Rosman *et al.*, 1994). This information, in addition to differences in the isotope ratios of the ores used for gasoline lead packages, provides a standard of comparison for environmental sample analyses.

Comparison of the different lead isotope ratios with lead concentrations provides the basis for the ALAS model calibration curve. By plotting one isotope ratio against the other, or a lead isotope ratio versus lead concentration, alleged patterns of data arise that can distinguish between multiple sources. This technique reportedly allows one to establish the time of formulation to within one to five years, depending on the slope of the ALAS model curve and calibration sample scatter (Hurst, 2000). Examples of the degree of resolution for different time periods using this analysis are  $\pm 1$  year for 1965 to 1980, and  $\pm 1.5$ –2 years for 1980 to 1990, with the larger errors occurring when the ALAS model ages exceed 1985 (Cline, Delfino and Rao, 1991; Hurst *et al.*, 1996, 1998a,b; 2000).

## Biomarkers

Biomarkers are organic compounds that are present in oils and source rocks that have carbon skeletons related to their functionalized precursors (Philp, 1998b). Most crude and Bunker C oils, for example, contain biomarkers, such as terpanes and steranes, that are resistant to biodegradation (Walker, Colwell and Petrakis, 1976). Because of their structures, these biomarkers represent a large number of different chemical compounds and isomers of the same compounds (Kaplan *et al.*, 1995).

Biomarkers used for source identification include  $C_2$ -dibenzothiophenes/  $C_2$ -phenanthrenes,  $C_3$ -dibenzothiophene/  $C_3$ -chrysene,  $C_{29}$ - $\alpha$ ,  $\beta$ -pentacyclic hopanes/  $C_{30}$ - $\alpha$ ,  $\beta$ -pentacyclic hopanes,  $C_{23}$ -tricyclic hopane/  $C_{24}$ -tricyclic hopane, and 4-methyldibenzothiophene/ 2-3-methyldibenzothiophene ratios (Wang, Fingas and Sergy, 1994; Wang and Fingas, 1995; Douglas *et al.*, 1996). The  $C_{30}$ -pentacyclic terpane (hopane) and certain tricyclic terpanes are among the most stable biomarkers in crude oil (Peters and Moldowan, 1993). Of the tetracyclic steranes, diasteranes are the most stable. For crude oil or heavy distillate fuels, pentacyclic triterpanes ( $C_{27}$ – $C_{35}$ ) and steranes ( $C_{27}$ – $C_{30}$ ) are commonly used due to their high molecular weight (Stout *et al.*, 1999a). For middle distillate fuels, biomarkers include bicyclic sesquiterpanes ( $C_{14}$ – $C_{16}$ ), acyclic regular isoprenoids ( $C_{13}$ – $C_{25}$ ), tricyclic diterpanes ( $C_{17}$ – $C_{20}$ ), aromatic diterpenoids ( $C_{18}$ – $C_{20}$ ), tricyclic terpanes ( $C_{19}$ – $C_{25}$ ), and various polycyclic aromatic hydrocarbons such as naphthalenes and phenanthrenes (Stout *et al.*, 1999a; Stout, Uhler and McCarthy, 1999).

## Degradation Models

Degradation models that are used for age dating are normally premised on a relationship based on a data set from which a particular degradation rate is postulated. This degradation rate is then used to

predict the known concentration of compound for an earlier period of time for which data is unavailable.

Numerous models exist for calculating the degradation rate of benzene, toluene, ethylbenzene, xylenes (BTEX) and other compounds. Assumptions that are routinely used in first-order biodegradation models for BTEX include: that the degradation rate that is uniform in time and space; that the first-order degradation rates do not depend upon the status of the *in situ* microbial population; and that contaminant loading rates and the toxic effects of contaminants are ignored (e.g. first-order degradation rates may only be valid over a portion of a concentration range) (Odermatt, 1994). An example in a one-dimensional idealization is (Buscheck and Alcantar, 1995; Brown *et al.*, 1997; Westervelt *et al.*, 1997):

$$\lambda = v_c/4\alpha_x([1 + 2\alpha_x(k/v_x)]^2 - 1)$$

where  $\lambda$  is the degradation rate,  $v_c$  is the contaminant velocity along the x-direction (adjusted for retardation),  $\alpha_x$  is the longitudinal dispersivity coefficient,  $k$  is the attenuation rate in units of time,  $v_x$  is the linear groundwater velocity and  $k/v_x$  describes the slope of the regression line fit to the log contaminant concentration data as a function of distance along the centerline axis of the contaminant plume (McNab and Dooher, 1998).

The difficulty in relying on this inverse solution relationship is that dispersivity can also produce concentration distributions that decline with distance from a continuous source. In many instances, especially when analyzing small numbers of data points, it is possible to fit a straight line through a log concentration versus distance axis with a high degree of correlation, even when degradation is insignificant or absent. A linear trend in log concentration values versus distance from the contaminant source is therefore not conclusive proof of the existence of transformation processes. Other potential biases include steady-state condition presumptions, inability to model fluctuations in source strength with time, heterogeneous flow and transport, non-alignment of monitoring well locations along the contaminant plume centerline, dilution effects due to well screen length, sampling and analytical bias, and non-uniform degradation rate distribution (McNab and Dooher, 1998, 1999).

## Contaminant Transport Models

Contaminant transport equations are frequently used as evidence for estimating the origin and age of a contaminant release. Issues that are potentially resolved with contaminant transport models include the estimation of when a contaminant was released at the ground surface, as well as when a contaminant entered the groundwater and/or crossed a property boundary. If a contaminant release occurred at the ground surface, the cumulative time required for the contaminant to migrate through the surface pavement (if present) and/or soil, prior to entering the groundwater, must be considered.



## Contaminant Transport through Pavement and Soil

### Pavement

If the contaminant has migrated through a paved surface prior to entering the soil column, the time required for this transport is usually important to the goal of determining when the fluid entered the groundwater. Information required for this evaluation includes the liquid and/or vapor density of the fluid, whether the release is steady-state or transient, pavement thickness, pavement permeability, porosity and moisture content, and the concentration of the fluid above, within and below the pavement prior to the release (Morrison, 1999c, 2000c). Depending on whether the dominant contaminant phase is vapor or fluid, numerous expressions are available in the literature that estimate transport time (Carslaw and Jaeger, 1959; Crank, 1985; McCoy and Rolston, 1992; Cohen, Mercer and Matthews, 1993; Choy and Reible, 1999).

Numerous challenges to contaminant transport through a paved surface are available. Some generic categories of those challenges include:

- variability of the model parameters (e.g. are they measured or reasonably assumed?);
- accuracy of the known circumstances of the spill event(s);
- environmental conditions at the time of the release(s) (e.g. thickness of the spill, composition, air temperature, etc.);
- consistency of the modeled results with measured contaminant results under the paved surface (if available);
- impact of potential short-circuiting pathways, such as expansion joints and/or cracks on the conceptual model; and
- availability of a physical sample of the paved surface and testing for physical properties, then consistency of input parameters for the model with the direct measurements.

Acquisition of a pavement sample and performance of direct measurements on that sample are advisable to attain representative physical measurements. The assumption that the building foundation consists of a monolithic layer of concrete may be incorrect. The European Chlorinated Solvents Association, for example, recommends that, at buildings that handle chlorinated solvents, a multi-layer construction consisting of a 5–10-centimeter-thick concrete layer covered with a barrier such as poly-*iso*-butylene or bitumen is implemented. The actual concrete construction is then built on this barrier (European Chlorinated Solvents Association, 2000). The author has observed the presence of plastic sheeting underlying a concrete foundation; the sheeting prevents moisture from seeping into the concrete and/or it isolates the concrete during placement/curing from a high water table. Another example of multi-layer construction is the building foundation that has multiple concrete pours, which create horizontal preferential pathways for contaminant transport between the concrete layers.

These types of features, if not addressed by the model, can jeopardize its scientific validity.

An understanding of the release circumstances is critical for creating a realistic conceptual model from which the mathematical description evolves. If the model ignores processes such as evaporation and/or assumes that the liquid thickness is constant, the transport rate results will be over-estimated. If cleanup activities (e.g. sawdust, green sand, absorbent socks, Sorball, crushed clay, etc.) are performed coincident with the release, or if the spill occurred in a building with forced air, then the competing processes will result in less liquid being available for transport through the pavement. The result is a slower transport rate, assuming that no preferential pathways are present.

### Soil

Hundreds of models are available that describe chemical transport through soil. An example of a one-dimensional equation describing the transport of a single compound via advection and diffusion in the unsaturated zone is presented to illustrate the basic structure of these types of expressions (Jury, Sposito and White, 1986; Jury and Roth, 1990):

$$R_l \partial C_l / \partial t = D_u \partial^2 C_l / \partial z^2 - V \partial C_l / \partial z - \lambda_\mu R_l C_l$$

where  $C_l$  is the pore water concentration in the vadose zone,  $\lambda_\mu$  is the decay constant,  $R_l$  is the liquid retardation coefficient,  $D_u$  is the effective diffusion coefficient, and  $V$  is the infiltration rate.

The retardation coefficient ( $R_l$ ) is estimated by:

$$R_l = \rho_{bu} K_{du} + \theta_\mu + (\phi_\mu + \theta_\mu) K_H$$

where  $\rho_{bu}$  is the soil bulk density,  $K_{du}$  is the distribution coefficient for the contaminant of interest,  $f_m$  is the soil porosity,  $\theta_\mu$  is the soil moisture content, and  $K_H$  is the Henry's constant for the contaminant of interest.

The distribution coefficient ( $K_{du}$ ) of the contaminant is given as:

$$K_{du} = 0.6 f_{oc,u} K_{ow}$$

where  $f_{oc,u}$  is the fraction of organic carbon in the soil and  $K_{ow}$  is the octanol-water partition coefficient for the contaminant of interest.

The degradation rate constant is described as:

$$\lambda_\mu = \ln(2) / T_{1/2\mu}$$

where  $T_{1/2\mu}$  is the degradation half-life of the contaminant of interest.

The effective diffusion coefficient is:

$$D_u = \tau_L D_{LM} + K_H \tau_G D_{GM}$$

where  $D_{LM}$  is the molecular diffusion coefficient in water,  $\tau_L$  is the soil tortuosity to water diffusion coefficient,  $D_{GM}$  is the molecular diffusion coefficient in air, and  $\tau_G$  is the soil tortuosity to air diffusion.



The tortuosity value associated with the diffusion of a compound in water and air is described by (Millington and Quirk, 1959):

$$\tau_L = \theta_\mu^{10/3} / \phi_\mu^2 \quad \text{and} \quad \tau_G = (\phi_\mu - \theta_\mu)^{10/3} / \phi_\mu^2$$

Challenges to contaminant transport through soil models include the impact on flow velocity of preferential pathways (e.g. dry wells, utility trenches, foundation borings, sewers and storm water piping backfill), colloidal transport (Villholth, 1999), contaminant fingering (Miller, Gleyzer and Imhoff, 1998) and co-solvent transport (Morrison and Newell, 1999). Other issues include the confidence levels associated with the model parameters that describe the soil (i.e. soil porosity, soil texture, organic matter content), hydraulic properties (gradient, saturated versus unsaturated flow), contaminant properties (fluid viscosity, mixture versus pure compound), phase state (vapor or liquid), and the circumstances of the release (volume of release, presence and/or composition of the paved surface, if any) (Morrison, 1999c). Another area of inquiry is whether the values used to describe various soil properties are obtained from literature, or measured at the release location. The author has observed that even soil properties measured at the site may be selected from locations other than from the vicinity of the release, and used in the model in order to obtain a prescribed result.

## Groundwater Models

The rate of contaminant transport in groundwater is routinely used as evidence in insurance litigation for source identification, age dating and cost allocation purposes. Models used to date contaminant releases range in sophistication from a straight line drawn between an alleged source and the leading edge of a contaminant plume to sophisticated three-dimensional contaminant transport models.

The origin of inverse modeling for contaminant transport in groundwater is pre-dated by research in the heat transfer literature (Huang and Ozisik, 1992; Bayo *et al.*, 1992; Silva-Neto and Ozisik, 1993). Issues regarding the use of inverse modeling for source identification are common to heat transfer and groundwater modeling. Governing equations in the heat transfer literature, for example, are similar to the advection-dispersion equations used in groundwater models, except that the advection term is seldom used in inverse heat conduction problems (Lattes and Lions, 1969; Alifanov and Artyukhin, 1976; Tikhonov and Arsenin, 1977). Issues regarding parameter confidence are also addressed in many heat transfer equations (Beck and Arnold, 1977; Alifanov and Neuarokomov, 1989; Marquardt and Auracher, 1990; Carasso, 1992).

### Inverse Groundwater Models

The term “backward extrapolation modeling” was reported in 1991 by Allen Kezsbom and Alan Goldman, in an article describing the *Sterling v. Velsicol Chemical Corporation* case (855 F.2d 1188 6th Circuit Court, 1988; Kezsbom and Goldman, 1991) and the term reverse, or inverse, modeling was used by

subsequent authors (Woodbury and Ulrych, 1996; Woodbury *et al.*, 1998; Erickson and Morrison, 1994; Morrison, 1998a,b, 1999a,c; Parker, 2000). In its simplest application, inverse modeling relies upon the observed length of a contaminant plume and an assumed groundwater velocity, in estimating the time that a contaminant has been in the groundwater. More sophisticated approaches use inverse models to reconstruct complex, multi-parameter release histories with known source locations from spatially distributed plume concentration data (Skaggs and Kabala, 1994, 1995, 1998; Woodbury and Ulrych, 1996).

The use of inverse modeling for parameter estimation and for source concentrations and timing is found in the groundwater literature (Neuman, 1973; Yeh, 1986; Ala and Domenico, 1992). In one inverse modeling application, a least squares method was used to identify the location and discharge rates of contaminants migrating from five disposal sites over a five-year period (Gorelick, Evans and Remson, 1983). Other approaches include identifying the contaminant source location with backward probability models to establish the most likely of several release sites. Bagtzoglou, Dougherty and Thompson (1992) described the use of a reverse time random particle method to estimate the probability that a particular site was the source of a contaminant plume. These probability approaches assume a single point source release (Birchwood, 1999). Wilson and Liu (1995) solved the advection-dispersion equation backward in time to construct source location probabilities, assuming a single point source release. In another application, the vertical concentrations of PCE and TCE in an aquitard were evaluated to reconstruct a release history. In this example, only diffusion and sorption were assumed to affect mass transport in the aquitard (Ball *et al.*, 1997; Liu and Ball, 1999). Dimov, Jaekel and Vereacken (1996) used the adjoint formulation of the one-dimensional advection-dispersion-deposition equation for source identification and loading rate. Another approach modeled contaminants from a constant source concentration using two-dimensional diffusion to estimate source characteristics and transport parameters from head and concentration data (Sonnenberg, Engesgaard and Rosbjerg, 1996). Sidauruk, Cheng and Ouazar (1997) developed a set of analytical procedures for contaminant source identification that relied upon contaminant concentrations measured within a two-dimensional contaminant plume. Contaminant flow was assumed to be homogeneous and groundwater velocity was uniform for instantaneous and continuous releases. The authors noted the limitations of certain parameters that can only be uniquely determined by sampling at a minimum of two different times.

The successful review of an inverse model includes analysis of the model selection, input parameters and computer code. Model components to be examined include:

- confidence limits associated with the selected physical and hydraulic parameters;
- selection of the boundary conditions and correlation with the actual hydrogeologic system;

- consistency of the groundwater flow direction and velocity over time;
- the validity of the hydraulic conductivity and/or transmissivity values and structure (e.g. the location of sampling points and the types of basis functions employed) (Sun and Yeh, 1985);
- assumptions used to determine when and where the contaminant entered the groundwater;
- loading rate(s) selected for chemicals entering into the groundwater;
- contaminant retardation and/or degradation rates (Davidson and Creek, 2000);
- identification of the leading edge of the contaminant plume (model-specific); and
- effect of recharge/discharge rates (if applicable) of water into the system.

Uncertainties associated with hydraulic and chemical parameters can be addressed by probabilistic simulation techniques (Woodbury and Liu, 1995). Probabilistic modeling involves utilizing user-specified probability distributions of physical and chemical model variables, based on available data, to produce forecasts regarding plume length and expansion rates through multiple Monte Carlo realizations. Inverse models incorporating probabilistic analysis are scientifically more defensible than approaches relying on unique values for these same parameters.

Some applications of inverse models for timing often require an accurate value for the length of the contaminant plume. If the location of the contaminant release into the groundwater and/or the leading edge of the contaminant plume is unknown or approximated, significant variations in the estimated age of the release occur. The distance to the leading edge of the contaminant plume is an inherently nebulous concept because of the highly irregular geometry of contaminant plumes. The irregular geometry is further exacerbated through biases created by monitoring well network configurations. As a result, it is necessary to define a standard protocol for defining the plume length (i.e. ND, 10 µg/L contour, MCL, etc.) or to prescribe a plume algorithm to estimate plume lengths directly from contaminant concentration data and well locations (McNab and Dooher, 1999).

When the contaminant plume length is measured, it is usually assumed that the contaminant plume is expanding at a consistent rate prior to when it is measured. The degradation of a compound, however, may result in daughter products with different retardation values than the parent compound that is no longer detected at the leading edge of the plume. Other considerations may include biased water level measurements from a monitoring well that is coincident with an activity, such as a pumping well that stresses the aquifer. These changes in water level are compared with the model results to ascertain whether they were incorporated into the model and, if so, the correlation between the modeled versus simulated water level measurements. Another option is to compare the input parameters of the inverse model with other site models for consistency (e.g. remediation models, risk assessment models). It is not uncommon that hydraulic and chemical properties selected for a Risk Based

Corrective Action (RBCA) model are different to those used in inverse modeling.

In some cases, the model sophistication requires a more rigorous examination to identify potential sources of bias (Snodgrass and Kitanidis, 1997; Skaggs and Kabala, 1994). Inverse models relying on a Fourier series approach to express a breakthrough curve, with the Fourier series expressed as functions of the release location and release history, for example, can contain substantial model resolution errors. Inverse models are often sensitive to the accuracy of the inferred source location as some prior knowledge of the release is usually required (Birchwood, 1999). The impact of the sampling location and frequency on model uncertainty, especially close to the source, where parameter uncertainty is significant, even at small concentrations, should be carefully examined. Another issue is the ability of the inversion scheme to filter out systematic and random measurement errors associated with the model parameters (Birchwood, 1999, 2000).

#### *Phase-separate models*

Inverse solutions are also used for phase-separate liquids with many of the same issues previously discussed. Butcher and Gauthier (1994), for example, estimated the residual DNAPL mass from down-gradient concentration data from a source, by using a simplified inverse modeling solution to estimate the source flux from monitoring well observations. The flux obtained from this solution was compared with the flux estimated from the mass transfer model of NAPL dissolution, to yield an estimate of NAPL volume and mass.

If an inverse model is used for source identification, a different set of governing equations and additional parameters are needed than for the same approach for a compound dissolved in the groundwater. For light non-aqueous phase liquid (LNAPL) transport along the water table, the movement can be described as (Parker and Lenhard, 1990):

$$Q_o = -T_o \nabla Z_{ao}$$

where  $Q_o$  is the vertically integrated Darcian velocity,  $T_o$  is the light non-aqueous phase liquid,  $Z_{ao}$  is the height at which the water and LNAPL capillary pressures are equal which corresponds to the LNAPL-air interface. The transmissivity of the light non-aqueous phase liquid is then described by (Parker and Lenhard, 1990):

$$T_o = \int_{Z_{o\psi}}^{Z_o} \rho_{ro} k_{ro} K_h / \eta_{ro} dZ$$

where  $Z_{o\psi}$  is the elevation where the water and light non-aqueous phase liquid pressures are equal,  $Z_o$  is the uppermost elevation at which mobile light non-aqueous phase liquid occurs,  $K_h$  is the horizontal saturated hydraulic conductivity relative to water,  $\rho_{ro}$  is the specific gravity of the LNAPL,  $k_{ro}$  is the relative permeability of the NAPL and  $\eta_{ro}$  is the light non-aqueous phase liquid to water viscosity ratio. The pore

velocity of the leading edge of the LNAPL at the water table ( $v_n$ ) is then defined as:

$$v_n = Q_o/V_{\text{LNAPL}}$$

where  $V_{\text{LNAPL}}$  is the mobile LNAPL volume per unit area.

A key variable in inverse modeling for a light non-aqueous phase liquid is the validity of the three-phase (air, water, NAPL) expression describing the pressure distributions between these fluids for a particular soil texture. If this expression is reduced to a monotonic nonlinear relationship, the legitimacy of this non-hysteretic expression requires scrutiny.

Issues for consideration when reviewing or constructing phase separate inverse models include the accuracy of values selected for fluid density, interfacial tension and soil texture. Fluid viscosity and density measurements are rarely measured. Published values can deviate significantly from field measurements due to weathering and/or co-mingling of the LNAPL with other compounds. If the measured thickness of a phase-separate liquid in a monitoring well is used in a phase-separate model, an opportunity for modeling error exists. For the measured LNAPL thickness in a monitoring well, uncertainty occurs when correlating the measurement to the actual LNAPL thickness in the formation (they are not identical). Numerous mathematical expressions are available to make the adjustment. Additionally, it is not uncommon for field measurement errors to be perpetuated in the model. For example, the thickness of a gasoline/diesel emulsion in a monitoring well may be reported as a LNAPL, resulting in an over-estimation of the actual LNAPL volume. The installation of a well and/or cone penetrometer test location between these wells, and comparison with the model, may be illustrative if this type of model bias is suspected.

LNAPL models normally assume that the phase-separate liquid is continuous and/or connected. If this assumption is incorrect, the LNAPL volume in the subsurface can be over-estimated. If monitoring wells are separated by hundreds of feet and the LNAPL thickness is thin (less than a foot), the possibility that the LNAPL is not continuous is highly probable.

## Conclusions

The application of the forensic techniques described in this paper for age dating and source identification should be carefully evaluated to determine if the results could provide information relevant to the issues in a case. In the context of environmental litigation, the results from each technique should be coupled with other groups of evidence, but not configured so as to jeopardize other lines of evidence if contradictory information is developed. The results of forensic techniques used for age dating and source identification should be able to withstand intense scientific scrutiny relative to the purpose for which the data was collected.

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## Appendix 1

Solvent and chemical formula	Chemical and commercial synonyms
Carbon tetrachloride (CCl <sub>4</sub> )	Chemical: carbon bisulfide; carbon bisulphide; carbon chloride; carbon disulphide; carbon sulfide; carbon sulphide; dithiocarbonic anhydride; methane tetrachloride; perchloromethane; sulphocarbonic anhydride; tetrachlorocarbon; tetrachloromethane. Commercial Synonyms: Benzinoform; Carbona (A. Klipstein & Company); Carbon chloride; Carbon tet; ENT 4,705; Fasciolin; Flukoids; Freon 10; Halon 104; Necatorina; Necatorine; Refrigerant 10; R10; RCRA waste number U211; Tetrachloormetaan; Tetrafinol; Tetraform; Tetrasol; UN 1846; Univerm; Vermoestricid; NCI-C04591; UN 1131; Weeviltox.
Chloroform (CHCl <sub>3</sub> )	Chemical: Formyl trichloride; Methenyl chloride; Methyl trichloride; Methenyl trichloride; Trichloride Trichloroform; Trichloromethane. Commercial Synonyms: Chloroforme (French); Choroformio (Italian) methyltrichloride; Methan; Freon 20; R 20; Refrigerant 20; Trichloormethaan (Dutch); Trichlormethan (Czech); Trichlorometano (Italian); UN 1888.
Chloromethane (CH <sub>3</sub> Cl)	Chemical: Methyl chloride; Monochloromethane. Commercial Synonyms: Arctic R40; Freon 40; UN 1063.
Dichloromethane (CH <sub>2</sub> Cl <sub>2</sub> )	Chemical: methylene bichloride; methylene chloride; methylene dichloride; methane dichloride; Chlorure de methylene; metylenu chlorek (National Institute of Standards and Technology, 2000) Commercial Synonyms: Aerothene MM (Dow Chemical Company—designed to solubilize a wide variety of polymeric materials dispensed from aerosol packages; also used for adhesive and paint stripping formulations); Cold Parts Cleaner (Immersion 609-pre ~1990 was about 30% methylene chloride); DCM; Freon 30; M-17 solvent; Methylene Chloride FCC/NF (Dow Chemical Company—used for extraction and processing in the food processing and pharmaceutical industries); Methylene Chloride Vapor Degreasing Grade (Dow Chemical Company—a low-temperature solvent for temperature-sensitive parts, such as cleaning air-gauged or manually-handled parts); MM Narcotil; NCI-C50102; Solaesthin; Solmethine; R30; RTECS; GY 4; Turco 5873; #5141 Chlorinated Solvent.UN1593.
Freon 11 (CCl <sub>3</sub> F)	Chemical: Fluorotrichloromethane; Monofluorotrichloromethane; Trichlorofluoromethane. Commercial Synonyms: Algonfrene Type 1; Arcton 9; Electro-CF 11; Eskimon 11; F11; FC 11; Fluorocarbon 11; Freon 11A; Freon 11B; Freon HE; Freon MF; Frigen 11; Genetron 11; Halocarbon 11; Isceon 11; Isotron 11; Ledon 11; Refrigerant 11; Ucon 11; Ucon fluorocarbon; Ucon Refrigerant 11.
Freon 113 (FCI <sub>2</sub> CCF <sub>2</sub> Cl)	Chemical: 1,1,2 trifluoro-1,2,2-trichloroethane; trichlorotrifluoroethane; 1,1,2-trichloro-1,2,2-trifluoroethane. Commercial Synonyms: Arcton 63; Arklone P; Blacotron TF; Daiflon S3; Fluorocarbon 113; F-113; FC-113; Freon 113; Freon TF; Frigen 113a; TR-T; Freon PCA; Genesolv D; Genetron 113; Halocarbon 113; Isceon 113; Isotron 113; Khladeon, Kaiser Chemicals 11; R113, Refrigerant 113; TTE; 113; Ucon-113; Ucon fluor.
Trichloroethylene (C <sub>2</sub> HCl <sub>3</sub> )	Chemical: Acetylene trichloride; ethylene trichloride; ethinyl trichloride; trichloroethylene; 1,1,2-trichloroethylene, trichloroethene; 1,1-dichloro-2-chloroethylene; 1-chloro-2, 2-dichloroethylene. Commercial Synonyms: Algylen; Alk-Tri (Dow Chemical Company); Anamenth; Anameneth; Benzinol; Blancosolv; Blacosolv; Cecolene; chlorylea; Chlorylen; Chlorilen; Circosolv; Crawhaspol; Densinfluat; Dow-tri, Dow-TriPhilex; Dukerson; DuPont Dry Clean; Dux Water Repellant; Ethyl Trichloroethylene; Ethinyl Tri-plus; Ethinyl trichloride; Ex-Tri (Dow Chemical Company); Fleck-flip; Flock-flip; Fluate; Germalgene; Germalgen; Hi-Tri (Dow Chemical Company-low inhibitor TCE that is ideal for formulations, extractions and catalyst processes that are sensitive to higher inhibitor concentrations); Instant Chimney Sweep Spray (Huff, 1971); Lanadin; Lash Bath False Eyelash Cleaner; Lethurin; M-17 solvent; Narcogen; Narkosoid; Neu-Tri (Dow Chemical Company-used in formulations, extractions and catalysts); NCI-C04546; Nialk Trichlor MD (Hooker Chemical Company); Nialk Trichlor MDA (Hooker Chemical Company); Nialk Trichlor X-1 (Hooker Chemical Company); Nialk Trichlor-Extraction (Hooker Chemical Company); Nialk Trichlor-Technical (Hooker Chemical Company); Petzinol; Perm-a-Chlor (Hooker Chemical Company—Detrex Inc); Perm-a-Chlor NA (Hooker Chemical Company—Detrex Inc); Perm-a-Chlor NA-LR (Hooker Chemical Company—Detrex Inc); Petzinol; Phillex (industrial grade); Sears Air Freshener; Stauffer; Sears Odor Neutralizer; Trethylene; Tri; Threthylene; Triad Metal Cleaner and Polish; Trichlor Type 113, 114, 115 and 112 (industrial grade); Tri-Clene (DuPont de Nemours Company, Diamond Shamrock); Trielene; Trichloran; Triclene (DuPont, Diamond Shamrock); Triclene D, L, LS, MD, ME, R, Paint Grade and High Alkalinity (DuPont, Diamond Shamrock);Trichloren; Triklone (industrial grade); Trilene (anesthetic grade); Triline; Triman (anesthetic grade); Trimar; Triline;Trethylene; trichloride Triad E (Hooker-Detrex); Tri-Paint Grade (industrial grade); Trimar; Trisan; Turco Surjex; Triasol (Trichlooretheen Dutch); Trichloraethen (German); Trichloran; Trichlorretent; Trichloroethylene Dual (industrial grade); Trichloroethylene Extraction Grade (industrial grade); Trichloroethilene and Trielina (Italian); Trivec; Tromex; tVestrol; UN 1710;Vapoclean; Vapoclor; Vitran; Vestrol; V-strol; Westrosol; Zip Grip Accelerator (Doherty, 2000).



Solvent and chemical formula	Chemical and commercial synonyms
Tetrachloroethylene (C <sub>2</sub> Cl <sub>4</sub> )	Chemical: Carbon bichloride; Carbon dichloride; ethylene tetrachloride; 1,1,2,2-tetrachloroethylene; tetrachloroethylene; perchloroethylene. Commercial Synonyms: Ankilostin; Antisol; Blacosolve No. 2; Crack Check Cleaner C-NF; Didakene; Dee-Solv; Dowper (Dow Chemical Company—a high purity grade solvent designed for drycleaning); Dow-clene ECENT 1,860; Fedal-UN; Gunk (Radiator Specialty Corporation); Isoform (Dow Chemical—used in refinery applications to re-activate catalyst where the catalyst is not sensitive to oxygen and nitrogen containing compounds); Midsolv; NCI-C04580; Nema: PCE; PER; PERC; Percelene; Perchloroethylene SVG Double Stabilized (Dow Chemical Company—highly stabilized solvent for heavy duty cleaning and metal degreasing where there is high contamination); Perchloroethylene Industrial Grade (Dow Chemical Company—used in brake cleaner formulations and adhesives); (Perawin; Perchlor; Perclene (DuPont; Diamond Shamrock); Percosolv; Perk; Persec and PerSec (Vulcan Materials Company); Per-Ex; Perm A Clean; Perklone (United Kingdom); Phillisolv; Tetlen; Tetrophil; Tetracap; tetrachloroethylene; tetrachloroethene; Tetraleno; Tetroguer; Tetropil; Tetravec (United States); UN 1897; #5141 Chlorinated Solvent ( <a href="#">Hardie, 1964</a> ); Wescosol (Westinghouse).
1,1-dichloroethylene (C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> )	Chemical: 1,1 dichloroethene; Sconatex. Commercial Synonyms: Chlorure de Vinylidene (French); 1,1 DCE; Chloride II; Vinylidene chloride; Vinylidene dichloride; VDC; Vinylidene
1,1-dichloroethane (C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> )	Chemical: ethylidene dinechloride; ethylened dichloride. Commercial Synonyms: Chlorinated hydrochloric ether; UN 2362.
1,2-dichloroethane (C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> )	Chemical: 1,2-bichloroethane. Commercial Synonyms: Borer sol; Brocide; 1,2 DCA; Destruxol borer-sol; Dichloremlusion; Dichlormulsion; Dichloroethylene; Dutch liquid; Dutch oil; Ethylene dichloride; Freon 150; EDC; ENT 1656; Glycol dichloride; NCI-C00511; UN 1184.
1,1,1-Trichloroethane (Cl <sub>3</sub> CCH <sub>3</sub> )	Chemical: alpha-trichloroethane; alpha-trichloromethane; chloroethene; methyl chloroform; methyltrichloromethane; trichloromethylmethane. Commercial Synonyms: Aerothene (Dow 1967—a methylene chloride and TCA propellant mixture); Ant Eater (96.5% TCA); Ani-Shield (33.1% TCA); Axothene No. 3 (Axtion-Cross Company); α-T; α-Trichloroethane; Aerothene; Aerothene TT; Alpha-; Amsco Solv 5620; Baltana; Barcothene Nu; Biosperse 4015 (3% TCA); Blakeothane; Blakesolve 421; Blaco-thane; CF2 Film Clean; Chloroethane NU; Chloroethene (1954) (Dow Chemical Company); Chloroethene VG, NU (Dow Chemical Company); Chlorten; Chloromane; Crack Check Cleaner C-NF; Dowclene ED (Dow Chemical Company, 1962); Dowclene WR (Dow Chemical Company, 1965 and used for cleaning microcircuitry and machined parts for the aerospace industry); Dyno-Sol; Genklene; DEV TAP; Devcon; Devon Metal Guard; ECCO 1550; Ethyl 111 Trichloroethane; Fire Ant “Quick Kill” (96.89% TCA); Fire Ant Killer (96.75% TCA); Fire Ant Killer and Nest Remover (96.5% TCA); FL-20 Flexane primer; Inhibisol; Insolv NU, VG; Kold Phil; Kwik-Solv; Lectrasolv 170; Lube-Lok 4253; Locquic Primer T; MCF; M-60; Methyl Chloroform Tech; Nacon 425; NCI-C04626; NU; One, One, One; Orlik Fire Ant Killer T (94% TCA); Penolene 643; Perm-Ethane DG; PCN UCD 5620; Rapid Tap; PCN-UCD 15620; Quik Shield; RCRA waste number U226; Saf-T-Chlor; Saf-Sol 20/20; Solvent M-50; Solvent 111 (Vulcan Chemical Company); Solventclean SC-A Aerosol; Stephenson Chemicals DDVP 20% (80% TCA); Strike (96.5% TCA); TCA; SKC-NF/ZC-73; Sumco 33; Trichem’s MC-96 (94% TCA); Tri-ethane Type 314, 315, 324 and 339 (PPG Industries); Triple One; Turco Lock; UCD 784; V-301; Vatron 111; VG; UN 2831; #10 Cleaner; #5141 Chlorinated Solvent.
Vinyl chloride (C <sub>2</sub> H <sub>3</sub> Cl)	Chemical: Chloroethylene; ethylene monochloride; monochloroethene; monochloroethylene. Commercial Synonyms: Chloroethene; VC; VCM; 1-Chloroethene; 1-Chloroethylene; MVC; Trovidur; UN 1086.

**Appendix 2***Uses of selected chlorinated solvents*

Chlorinated Solvent	Applications
Carbon Tetrachloride	An azeotropic agent for drying spark plugs, a delousing agent, used in dry/plasma etching, petroleum refining and pharmaceutical manufacturing. An extractant for oils from seeds, flowers, grease from hides and bones, and alkaloids from plants. Used as a solvent in the de-inking of paper, in liquid chromatography and in the manufacture of rubber. An ingredient in furniture polishes, floor waxes, paints and varnish removers.
Chloroform (trichloromethane)	Solvent for cleaning electronic circuit boards; product of chlorination from water treatment; preparation of fluorocarbon refrigerants and plastics; soil fumigant; insecticide solvent; preparation of refrigerants; rubber manufacturing; solvent for fats, oils, rubber, waxes and resins. Used in toothpaste and liniments. An extractant and purification of penicillin and other antibiotics. An intermediate for refrigerants and propellants. A fumigant for soil and prevention of mildew on tobacco seedlings. A general solvent and reaction medium. A solvent for dry-cleaning and used to recovery fat from waste products. Used in the extraction of essential oils, and of alkaloids from natural substances. A solvent for gums, resins, waxes and rubber. In pharmaceutical preparations it is used in cough syrups, expectorants, liniments, sedatives, carminatives, analgesics and anesthetic preparations. Used in the organic preparation of Freons, dyes and drugs. An ingredient in laundry starch preparations and miscellaneous paint related products.
Chloromethane (methyl chloride)	A natural product in sea water, coolant and refrigerant, herbicide and fumigant, used in the manufacture of silicone polymer pharmaceuticals/tetraethyl lead/synthetic rubber/methyl cellulose/agricultural chemicals/methylene chloride/carbon tetrachloride, methyl cellulose and chloroform, fluid for thermometric and thermostatic equipment. A refrigerant for household and small commercial refrigerators. A catalyst solvent for low-temperature polymerization. Used in aerosols of insecticides and plant hormones. Used in the extraction of natural food-flavoring materials. An actuating liquid in thermostatic controls. Rectification of salt baths for annealing metals. A methylating agent. Used in the preparation of quaternary ammonium compounds, ethers, esters, hydrocarbons and methyl silicone chlorides.
Chlorobenzene	A solvent for ethylcellulose, resins, paints, varnishes and lacquers. Used in the synthesis of phenol, DDT, aniline, picric acid, chloro and nitrochloro-benzenes, sulfur dyestuffs, military poison gas, drugs and perfumes. A solvent used in the production of rubber, resins, drugs, perfumes, and paints as well as a heat transfer medium. A component in fast-drying inks. A solvent carrier used in dyeing synthetic fibers and a component in household cleaning agents.
1,1-Dichloroethane (1,1-DCA)	A transformation product of TCA. An ingredient of paint, rubber cement, insecticides, fumigants, varnish and finish removers. Used in the manufacture of vinyl chloride and TCA. An ingredient in some lubricating oils ( <a href="#">Environmental Defense Fund, 2000</a> ).
1,2-Dichloroethane (1,2-DCA)	Gasoline additive; chemical intermediary; solvent; insecticide; seed fumigant; manufacture of acetyl cellulose; manufacture of vinyl chloride; solvent for rubber/resin/gums/waxes/fats and oils.
1,1-Dichloroethene (1,1-DCE)	A hydrolysis product of TCA and degradation product of PCE and TCE. Used as a chemical intermediate in vinylidene fluoride synthesis. An ingredient in coating resins, synthetic fibers and adhesives. Used in dyes, plastics, perfume, paint and adhesive manufacturing. A primary constituent in the Saran-type plastics (e.g. co-polymerized with vinyl chloride).
1,2-Dichloroethene (1,2-DCE)	A reduction product of TCE. Used as an industrial solvent in the manufacture of dyes, plastics, perfumes and lacquers. A solvent for oils, gums, resins, waxes, rubber shellac and cellulose acetate. Used in the extraction of dyes and perfumes and in lacquers, thermoplastics and rubber.
Freon-11 (trichlorofluoromethane)	A refrigerant; blowing agent for polyurethane foam; fire extinguishing; aerosol propellant; solvent. An ingredient in hair preparations, scatter rugs, bathmats, and specialty performance sealants ( <a href="#">Environmental Defense Fund, 2000</a> ).
Freon-113 (trichlorotrifluoroethane)	Used in fire extinguishers. A dry cleaning solvent. A feedstock in the production of other chlorofluorocarbons (e.g. chlorotrifluoroethylene). Used to strip flux from printed circuit boards (often combined with alcohol). A vapor degreasing solvent. An ingredient in some aerosols. Type I CFC-113 is intended for use in the cleaning of space vehicle components, precision assemblies, oxygen systems and electronic equipment and/or precision parts in clean rooms. Type II and IIA designations are typically used in vapor degreasing. An ingredient in synthetic resins and adhesives.

Chlorinated Solvent	Applications
Methylene Chloride (dichloromethane)	A secondary blowing agent used in the production of low density flexible polyurethane foam used to produce upholstered furniture/bedding and carpet underlay. An extractant for decaffeinated coffee and as an extraction solvent for hops. An ingredient in pill coating of pharmaceuticals (in Western Europe in 1994, accounted for 41% of total usage) (ECSA, 1997). A carrier solvent and reaction medium in the pharmaceutical industry. An inactive ingredient in pesticide formulations and in adhesive formulations used to bond contact cements for wood, metal and upholstered furniture. A process solvent for cellulose esters, polycarbonate, triacetate and triacetate ester production. Used in glues for welding plastic parts. A paint stripper in the aerospace industry. A solvent for cleaning paint booth, paint lines and spray guns. Used in paint stripping due to its ability to penetrate, blister and lift most types of durable finishes (Dow Chemical Company, 2000a) Used in food processing. An adhesive in mining applications. A photoresist stripper in the manufacture of printed circuit boards. A refrigerant used in low pressure ice and air-conditioning machines. A low temperature extractor of essential oils and edible fats. A solvent for removing oil, wax, paint and a selective solvent on various cellulose acetates. An ingredient in automotive parts cleaners.
1,1,2,2-Tetrachloroethane (1,1,2,2-TCA)	A solvent for oils, fats, waxes, resins, cellulose acetate, rubber, phosphorus and sulfur. An intermediary in the manufacture of trichloroethylene, perchloroethylene and other C2 chlorohydrocarbons. Used in soil sterilization, weed control and as an insecticide. A degreasing agent. Used in the manufacture of paint remover, varnish, lacquer, and photographic film. An ethyl alcohol denaturant.
Tetrachloroethylene (PCE)	A dry cleaning fluid of clothing, metal degreaser, solvent for waxes, grease, fats, oil, and gums. Used in printing ink manufacturing. An ingredient in paint removers. A feedstock in the production of CFC-113 and of hydrofluorocarbon refrigerant 134a and hydrochlorofluorocarbon 123, 124, 125, 142b and 141b (HSIA, 1999). An ingredient in maskant coating used to protect surfaces from chemical etchants in the aerospace and electronics industry. An ingredient in paper coatings and silicones. An ingredient in automotive parts cleaners, carburetor cleaning products and aerosol brake cleaners (along with PCE, methylene chloride, dichlorobenzene and cresylic acid, especially in pre-1974 formulations-PCE present at 90% in some brake parts cleaners). Present in some electrical transformers as a substitute for PCBs (HSIA, 1994, 1999). Used in the manufacture of detergents. An extraction solvent for vegetable and mineral oils. Used as an ingredient for military smoke screens (chlorobromomethane) in World War I and II (Kirk and Othmer, 1949; Brandt, 1997).
1,1,1-Trichloroethane (1,1,1-TCA)	Used in the production of vinylidene chloride, a primary solvent used for cold cleaning; and used in the photoresist process for developing and stripping electronic circuit boards. An ingredient in aerosol pesticides, adhesive formulations, coatings for wood furniture, metal substrates, traffic paints for signs and road lines, and an inactive ingredient in pesticide formulations. Used in California after 1988 as a blowing agent in the production of flexible foam used to make upholstered furniture, bedding and carpet underlays. A solvent for fats, resins, and waxes. An ingredient in aerosols; textiles; ink, oven cleaners, adhesives and correction fluid formulations (Avidado <i>et al.</i> , 1976). Used in the manufacture of plastics and metals. Used to clean printing presses, missile components paint masks, photographic film, printed circuit boards, plastic molds, motors, generators, appliances, and to clean leather and suede garments. An ingredient in spray and solid pesticides, rodenticides, drain cleaners, carpet glues, and fire ant insecticides (Environmental Defense Fund, 2000). A feedstock for the synthesis of hydrochlorofluorocarbons. An ingredient in brake parts cleaners.
1,1,2-Trichloroethane (1,1,2-TCA)	An intermediate used in the production of copolymer vinylidene chloride thermoplastic resins. A solvent used for oils, fats, waxes, cellulose, esters, tars, alkaloids, and resins. A solvent used for bonding acrylate plastics. Used in the extraction of natural products and for extracting acetone from aqueous solutions. A soil fumigant. A freezing-point depressant for carbon tetrachloride. A metal degreaser.
Trichloroethylene (TCE)	A metal degreasing solvent and a solvent for waxes, greases, fats, oils and gums. An ingredient in paint removers. A solvent base for metal phosphatizing systems. Used to degrease aluminum and for cleaning sheet and strip steel prior to galvanizing. Used to clean liquid oxygen and hydrogen tanks. An ingredient in grain fumigants (Huff, 1971). Used to degrease bones for making glues. An intermediate in the preparation of perchloroethylene, polyvinyl chloride, chloroacetic acid, hydrofluorocarbons, and fertilizers (Archer, 1996). A low temperature heat-transfer fluid. A freezing-point depressant in carbon tetrachloride based fire-extinguishing fluids. Used in the manufacture of detergents, dye intermediates, dyestuffs, leather, organic chemicals, paint, perfume, pharmaceuticals, rubber and varnish. A general anesthetic and an analgesic in dental extractions, childbirth short surgical procedures (Doherty, 2000). A dry cleaning spotting agent (Environmental Defense Fund, 2000).
Vinyl chloride (chloroethene)	A reduction product of 1,1- and 1,2-DCE. A gas used in the manufacture of polychloride vinyl (PVC) pipes, wire coatings; refrigerants, automobile upholstery, and copolymers. An ingredient in adhesives for plastics, extraction solvents and plastic house-wares. Used in the preparation of polyvinyl chloride and other polymers/copolymers such as Flamenol, Koroseal, Vinylite (alone or together with vinyl acetate or vinyl acetate and maleic anhydride), Geon (alone or together with vinylidene chloride), Tygon (with vinyl acetate), Velcon (with vinylidene chloride) and Saran (with vinylidene chloride) (American Insurance Association, 1972). Used in the pulp and paper industries as an impregnation agent (Environmental Defense Fund, 2000).